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14. ABSTRACT

Recent studies have been increasingly utilizing fluoroalkyl-substituted Polyhedral Oligomeric SilSesquioxanes (POSS) molecules, known as fluoroPOSS, for producing non-wetting surfaces. Most commonly, $(1H,1H,2H,2H\text{-perfluorodecyl})_8Si_9O_{12}$ (fluorodecyl POSS, has been utilized for its extraordinarily low surface energy (≈10 mN/m) and phase behavior in polymer blends. However, fluoroPOSS surfaces can seldom experience abrasion, or extended exposure to certain liquids, and still retain their non-wetting properties. A route to synthesize a functional fluoroPOSS molecule or monomer, with the ability to be covalently attached to a textured surface or polymer, is desired for the potential ability to develop a mechanically robust omniphobic surface. In the current study, mono-, di-, and tri-chlorosilanes tethered to a fluorodecyl POSS cage are synthesized *via* hydrosilylation of (vinyl, methyl) $(1H,1H,2H,2H\text{-perfluorodecyl})_8Si_9O_{13}$ POSS. Products are identified by NMR spectrometry. The synthesized monochlorosilyl-functional fluoroPOSS compound is subsequently used to treat silicon dioxide surfaces. Covalent attachment is confirmed by atomic force microscopy and dynamic contact angle analysis.

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FLUOROPOSS MONOLAYERS COVALENTLY BOUND TO A SILICA SURFACE

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Abstract

Recent studies have been increasingly utilizing fluoroalkyl-substituted Polyhedral Oligomeric SilSesquioxanes (POSS) molecules, known as fluoroPOSS, for producing non-wetting surfaces. Most commonly, (1H,1H,2H,2H-perfluorodecyl)$_8$Si$_8$O$_{12}$ (fluorodecyl POSS), has been utilized for its extraordinarily low surface energy (≈10 mN/m) and phase behavior in polymer blends. However, fluoroPOSS surfaces can seldom experience abrasion, or extended exposure to certain liquids, and still retain their non-wetting properties. A route to synthesize a functional fluoroPOSS molecule or monomer, with the ability to be covalently attached to a textured surface or polymer, is desired for the potential ability to develop a mechanically robust omniphobic surface.

In the current study, mono-, di-, and tri-chlorosilanes tethered to a fluorodecyl POSS cage are synthesized *via* hydrosilylation of (vinyl, methyl)(1H,1H,2H,2H-perfluorodecyl)$_8$Si$_9$O$_{13}$ POSS. Products are identified by NMR spectrometry. The synthesized monochlorosilyl-functional fluoroPOSS compound is subsequently used to treat silicon dioxide surfaces. Covalent attachment is confirmed by atomic force microscopy and dynamic contact angle analysis.

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Introduction

Polyhedral Oligomeric SilSesquioxanes (POSS) are a class of molecules consisting of a polyhedral Si-O core, surrounded by organic functionality. Recent studies have been increasingly utilizing molecules known as fluoroPOSS, which possess fluoroalkyl groups on their periphery, for the improvement of low surface energy characteristics. Most commonly, (1H,1H,2H,2H-perfluorodecyl)$_8$Si$_8$O$_{12}$ (fluorodecyl POSS), is used to produce non-wetting surfaces.[1-5] The utility of this compound stems from its extraordinarily low surface energy (≈10 mN/m), believed to be the lowest of any crystalline solid, as well as its phase behavior in polymer blends.[2] The structure of fluorodecyl POSS can be seen in figure 1. A common approach to produce a non-wetting surface using fluoroPOSS is to coat a pre-textured surface with a fluoroPOSS/polymer blend, or to deposit the blend on a flat surface in a specific way, such as electrospinning or spraying, to induce a specific texture. Depending on the texture of the surface and the particle loading concentration, surfaces utilizing fluoroPOSS can exhibit a wide range of non-wetting characteristics, from moderately hydrophobic to omniphobic, repelling essentially all liquids. Although these coatings have a wide range of applications, fluoroPOSS surfaces can seldom experience abrasion, or extended exposure to certain liquids, and still retain their non-wetting properties. A route to synthesize a functional fluoroPOSS molecule or monomer, with the ability to be covalently attached to a textured surface or polymer, is desired for the potential ability to develop a mechanically robust omniphobic surface.

In the current study, mono-, di-, and tri-chlorosilanes tethered to a fluorodecyl POSS cage are synthesized *via* hydrosilylation of (vinyl, methyl)(1H,1H,2H,2H-perfluorodecyl)$_8$Si$_9$O$_{13}$ POSS. Products are identified by NMR spectrometry, observing ^{1}H, ^{13}C, ^{19}F, and ^{29}Si nuclei. The synthesized monochlorosilyl-functional fluoroPOSS compound is subsequently used to treat silicon dioxide surfaces. Atomic force microscopy, reflectance spectroscopy and dynamic contact analysis are used to characterize covalently bound fluoroPOSS monolayers on the surface of silicon dioxide.

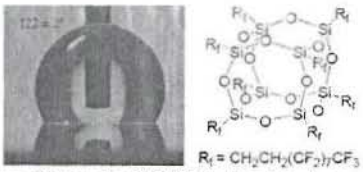

Figure 1. Structure of fluorodecyl POSS (left) and an image of a water droplet advancing on a silicon wafer spin-coated with fluorodecyl POSS.

Experimental

Materials. Dimethylchlorosilane, methyldichlorosilane, and trichlorosilane were obtained from Gelest and distilled prior to use. Platinum(0)-divinyl tetramethyldisiloxane (2 wt% Pt solution in xylene) was received from Aldrich. Hexafluorobenzene was used as received from Synquest Laboratories. Silicon wafers (25.4 mm diameter, Type N, 100) were obtained from Wafer World.

Instrumentation. ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra were recorded on a 300-MHz Bruker spectrometer. Wetting behavior of treated silicon substrates was performed on a DataPhysics OCA 20 goniometer. The rms roughness values of treated surfaces were obtained using an atomic force microscope (Digital Instruments Dimension 3100).

Synthesis of (vinyl, methyl)(1H,1H,2H,2H-perfluorodecyl)$_8$Si$_9$O$_{13}$ POSS (1). The synthesis of compound (1) will be discussed in a future publication.

Synthesis of (methyl, ethylchlorosilyl)(1H,1H,2H,2H-perfluorodecyl)$_8$Si$_9$O$_{13}$POSS (2a-2c). Compounds 2a, 2b, and 2c were prepared by the platinum-catalyzed hydrosilylation of compound (1) and dimethylchlorosilane, methyldichlorosilane, or trichlorosilane, respectively. The reaction scheme can be seen in Figure 2. A solution of compound (1) (0.5 g, 0.123 mmol) was sealed in a glass pressure vessel equipped with a built-in septum. The Pt catalyst (1.4 µL of 2 wt% solution) was then added to the solution *via* syringe. With the reaction mixture stirring at room temperature, 1 mmol of the appropriate silane was added *via* syringe. The reaction mixture was then allowed to stir for 24 hours at 100 °C. After cooling, solvent and excess silane were removed by dynamic vacuum, leaving a beige solid compound.

Results and Discussion

Synthesis. Mono-, di-, and tri-chlorosilyl functional fluoroPOSS molecules were synthesized by the hydrosilylation of (vinyl, methyl)-(1H,1H,2H,2H-perfluorodecyl)$_8$Si$_9$O$_{13}$ POSS and dimethylchlorosilane, methyldichlorosilane, or trichlorosilane, as shown in figure 2.

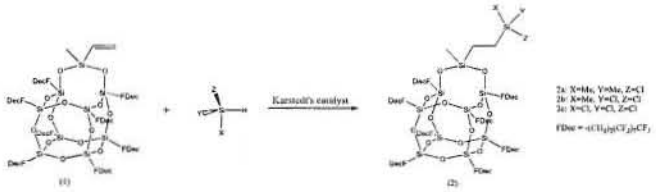

Figure 2. Synthesis scheme for chlorosilyl-functional fluoroPOSS.

Oxide Surfaces treated with chlorosilyl-functional fluoroPOSS. To qualify the use of the newly synthesized chlorosilyl-functional fluoroPOSS in non-wetting surfaces, (2-dimethylchlorosilylethyl, methyl)(1H,1H,2H,2H-perfluorodecyl)$_8$Si$_9$O$_{13}$ (2a) was used to treat a flat silicon dioxide surface. Once treated, dynamic contact angle analysis was used to characterize the wetting properties of the silicon wafers. This data, along with reflectance IR spectral data, confirms covalent attachment to the silica surface. The resulting surfaces are believed to be more thermally stable and mechanically robust than any other surface utilizing fluoroPOSS molecules. The wetting properties of covalently bound fluoroPOSS monolayers are also compared to that of spin coated surfaces. Previous research has used contact angles of various wetting liquids on (1H,1H,2H,2H-perfluorodecyl)$_8$ Si$_8$O$_{12}$ POSS spin-coated surfaces with extremely low rms roughness values to calculate the surface energy of the compound.[2] Variations in the wetting properties of covalently-bound fluoroPOSS derivatives and spin-coated R$_{f8}$ Si$_8$O$_{12}$T$_8$ POSS provide insight into the source of the low surface energy of the crystalline T$_8$ POSS compound. The use of chlorosilyl-functional fluoroPOSS molecules in treating oxide surfaces and other systems, such as polymers and macromolecules, will be the subject of future research.

Conclusions

Previously unreported chlorosilyl-functional fluoroPOSS molecules have been synthesized *via* hydrosilylation reactions. Synthesized compounds present a possible route for producing mechanically robust non-wetting surfaces. The monochlorosilyl-functional fluoroPOSS was used to covalently attach fluoroPOSS nanoparticles to a silicon dioxide surface. Spectral data and wetting properties of the treated surface confirm covalent attachment.

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